Kinetic Monte Carlo simulation of electrodeposition of polycrystalline Cu

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ABSTRACT

A two-dimensional cross-sectional poly-lattice kinetic Monte Carlo (2DCSP-KMC) model has been developed for simulation of the electrodeposition of polycrystalline copper on a copper and gold substrate. The mis-orientation and higher energetic state of grain boundaries are taken into account by introducing a 'strange' coordination number and a correction coefficient while determining the diffusion rate. The evolution of the microstructure, the average grain size, the variance of grain size and the distribution of grain-boundary mis-orientation of the deposit are also considered in simulations. The model has proven capable of capturing some key aspects of nucleation and growth mechanism including the nucleation type (e.g. homogeneous or heterogeneous), texture development, the growth of grains and higher energetic state of grain boundaries. The simulated microstructure qualitatively agrees with our experimental observation on the copper deposition on gold.

1. Introduction

Electrodeposition has found a wide range of applications in the fabrication of micro- or nano-patterns in electronic devices. Deposits of a wide variety of microstructures ranging from single crystal [1] to nano-crystal [2] have been obtained by electrodeposition using different deposition parameters and assisting techniques. It is imperative to understand the growth mechanism of the electrodeposit in order to tailor specific microstructure for various applications. Kinetic Monte Carlo (KMC) simulation has become a powerful tool for the study of electrocrystallization and is essentially the only feasible way of simulating the crystal growth at a practical size and time scale. It has been employed to simulate early-stage electrocrystallization at the both only the atomic scale or coupled to macroscopic models e.g. finite element or finite difference models for a multi-scale simulation of electrodeposition process. A detailed review on the KMC models for electrocrystallization can be found in our recent paper [3]. All those KMC models have one assumption in common: all atoms are forced to be deposited onto or jump to the sites of a single lattice. Strictly speaking, such single-lattice models are only suitable for simulation of single-crystal electrocrystallization because the important features of a polycrystalline structure, including the texture development and grain-boundary mis-orientation, cannot be captured in such models.

Although most electrodeposits of practical interests are polycrystalline, there have been few KMC models available for treating the electrodeposition of polycrystalline metals [4,5] and they are rather basic, simply associating a property representing several typical orientations with sites of a single lattice. This preliminary solution is also of interest in the simulation of polycrystalline Al [6] films, Cu [7], and Si [8] films by other thermal deposition processes. A major limitation of this approach is that the key aspects of grain boundaries, such as the high density of vacant sites and high energetic state, cannot be included. Bruschi et al. [9] developed a 'real' poly-lattice KMC model that represents the first monolayer of a polycrystalline film at two dimensions. Obviously, this 2D model is restricted to the early-stage deposition, i.e. before the full coverage of the substrate is reached. Huang et al. [10,11] developed a multi-lattice model by mapping a given number of lattices representing grains onto a single reference lattice for simulation of sputtering Al film. Rubio et al. [12] broadly extended Bruschi's 2D model to three dimensions, allowing atoms to diffuse across grain boundaries and change grain membership, but it gives a definite number of lattices such as Huang et al. reported. However, the higher energetic state at a grain boundary is still not considered. And pre-setting a definite number of lattices renders these multi-lattice models incapable of dealing with the nucleation process.

In the last decade, KMC simulation for polycrystalline growth has attracted increasing attention in the area of multi-lattice KMC models that have encountered various limitations. Neither grain-boundary mis-orientation nor poly- or even multi-lattice KMC models in simulation of electrodeposition have yet to be considered. In this paper, we develop a 2D cross-sectional poly-lattice

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(2DCSP) KMC model to simulate electrodeposition of polycrystalline copper, furthering our recent 2DCS-KMC model [3] for single-crystal electrocrystallization. This is understood to be the first attempt of using a poly-lattice KMC model to simulate the electrodeposition process. This leads to several advancements in the multi-lattice KMC models that have been developed for the thermal deposition processes in two aspects. Firstly, the energetic state of grain-boundary atoms due to mis-orientation is taken into account. Secondly, grains are generated on an ad hoc basis, as in real life, thereby no restriction is given to the number of lattices, which enable the model to treat the early-stage nucleation and grain growth at later stages as a whole process. Finally, the evolution of microstructure, grain statistics and grain-boundary mis-orientation distribution during the electrodeposition of copper on a copper or gold substrate can also be understood through the simulation, thereby the entire growth history of electrodeposits can be re-constructed based on the proposed growth mechanism.

2. Description of the model

The proposed model represents the cross-section of an idealized electrodeposition system consisting of cupric ions, Cu^{2+}, of a given concentration, deposited Cu atoms on either a Cu or Au substrate. Initially, a list of available sites on the substrate is pre-defined randomly. When a Cu atom is deposited on a substrate site, a new 2D triangular lattice (i.e. a (1 1 1) plane of a face-centred cubic lattice) representing a grain is generated and a random orientation (defined as the tilt angle of the lattice against the surface normal direction) between $0°$ and $60°$ is assigned. At the same time, the newly deposited atom induces up to six neighbouring lattice sites, which must either have at least two neighbouring atoms by considering that an atom with fewer than two neighbour atoms is unstable or be on/near the substrate (i.e. the distance to the substrate surface is less than the lattice constant a). Meanwhile, any neighbouring site that belongs to the other grains or substrate site within the range of the inhibiting distance $d_{inh}(= 0.8a)$ is annihilated, taking into account the steep increase of repulsive strength arising when the interatomic distance is progressively reduced. The deposition rate is computed by

$$r_{dep} = kC_{Cu^{2+}}e^{-\alpha nF\eta/RT} \qquad (1)$$

where k is the rate constant, $C_{Cu^{2+}}$ the concentration of Cu^{2+}, α the charge transfer coefficient, n the electron number, F the Faraday constant, η the overpotential, R the ideal gas constant and T the temperature. A deposited atom can diffuse to one of its nearest neighbour sites within its own grain or to a site belonging to other grains within the range of a and change its grain membership. This enables the simulation of grain-boundary dynamics at the atomic scale. The diffusion rate is computed by

$$r_{def} = w \cdot e^{-(e_{mig}+\Delta E)/Rt} \qquad (2)$$

where w is the jump frequency for diffusion, E_{mig} is the migration energy. $\Delta E = E_f - E_0$ is the difference between the energy of the system after and before the diffusion if the difference is positive and $\Delta E = 0$ if negative. E_{mig}, E_f and E_0 are determined by $E_x = N_{cord}E_{barr} + N_{cord}^{str}(\lambda E_{barr})$, where E_x represents E_{mig}, E_f or E_0, E_{barr} stands for the energy barrier for a Cu–Cu or a Cu–Au bond and N_{cond} is the coordination, counting the nearest neighbour atoms within the same grain. Here, we introduce a 'strange' coordination N_{cond}^{str}, counting the number of neighbours of the diffusing atom belonging to other grains within the range of a, and a correction coefficient λ (assumed to be 0.5) to treat the higher energy of the grain-boundary atoms. The values of other physicochemical parameters and the algorithm for event selection and KMC clock increment are described in our recent paper [3].

3. Results and discussion

The evolution of the microstructure of Cu deposit on Cu and Au substrate is illustrated in Fig. 1. As can be seen in Fig. 1a, a number of nuclei are evenly distributed across the Cu substrate on the deposition of 0.5 equivalent monolayer (EML) Cu atoms, which indicates a homogeneous nucleation. Upon the deposition of 5 EML these nuclei have grown into grains after impingement. These grains continue growing competitively both longitudinally and laterally. As a result, some of the grains are suppressed by their neighbours growing over them on 20 EML. Consequently, the suppressed small grains remain while others proceed with upward and competitively lateral growth. Finally on 50 EML, the deposit shows fabric texture with some finer grains near the deposit/substrate interface. In contrast, the microstructural evolution of the copper deposits on Au presents the characteristics of heterogeneous nucleation and growth as illustrated in Fig. 1b. It can be seen that a prominent grain stands out within 1 EML followed by another one in the next 4 EML, although no preferential nucleation site on the substrate is preset initially in the model. Before the saturation of the nucleation, the growth is basically dominated by a few grains which nucleate one after another at certain intervals. The resultant grains are, in average, much larger than on Cu substrate. Similarly, the grain growth after impingement follows the same mechanism of competitive growth as on Cu substrate, as indicated by the suppressed grains.

Individual grains are tracked in the simulation and post-analyzed statistically. The grains consisting of fewer than five atoms are not counted in the statistics considering their negligible volume fraction. The quantitative description of the grain growth history is presented in Fig. 2. The grain density soars to a saturation value at 8.1×10^8/m within about 0.4 s for the deposition on Cu substrate while for Au substrate it takes eight times as long to climb to a one-fourth saturated grain density as shown in Fig. 2a. We define an effective grain size $d = \sqrt[3]{(6NV_m/N_A\pi)}$, where N is the number of atoms in an individual grain, V_m the molar volume of the solid phase (0.71×10^{-6} m³/mol for copper [13]) and N_A the Avogadro's constant. The average effective grain size as a function of time is plotted in Fig. 2b. The saw-toothed part of the curve for Cu substrate and the stepped one for Au substrate is due to the intermittent nucleation events and the subsequent dominant growth of the large grains as described above. Normal grain growth generally obeys the power law $r^m - r_0^m = K_0t$ where r_0 is the initial grain size, m is a material-dependent growth exponent, K_0 the a temperature-dependent grain growth rate [14]. Least-square regression was performed based on the simulated data of the average grain size, through which it was found that $m = 2.53$, $K_0 = 4.66 \times 10^{-10}$ m/s for Cu substrate and $m = 2.53$, $K_0 = 8.75 \times 10^{-10}$ m/s for Au substrate. The variance of grain size also increases with the growth of grains as shown in Fig. 2c. It can be seen that the curve of the variance of grain size versus time fits perfectly well with the power law with an exponent of 1.265, exactly half the value of m, which further verifies the effectiveness of the regression analysis on the average grain size. The grain-boundary mis-orientation is also considered by simulation. As can be seen in Fig. 2d and e, overall, there are more low-angle boundaries ($0–12°$) for both substrates although the orientation of a grain is assigned completely stochastically on deposition of its first atom. The preference on low-angle boundaries is probably attributed to their lower energy as compared to high-angle boundaries. In terms of the distribution over time, the number of grain boundaries of a certain range of mis-orientation increases before reaching 20 EML for deposition on Cu and 30 EML for Au respectively and basically stabilizes afterwards.